September 2, 2004

Thomas M. Gray, M.S., D.A.B.T.
Senior Toxicologist
The American Petroleum Institute
Petroleum HPV Testing Group
1220 L. Street N.W.
Washington, DC 20005

Dear Dr. Gray:

The Office of Pollution Prevention and Toxics is transmitting EPA's comments on the robust summaries and test plan for the Reclaimed Substances Category posted on the ChemRTK HPV Challenge Program Web site on January 20, 2004. I commend The American Petroleum Institute Petroleum HPV Testing Group for its commitment to the HPV Challenge Program.

EPA reviews test plans and robust summaries to determine whether the reported data and test plans will provide the data necessary to adequately characterize each SIDS endpoint. On its Challenge Web site, EPA has provided guidance for determining the adequacy of data and preparing test plans used to prioritize chemicals for further work.

EPA will post this letter and the enclosed comments on the HPV Challenge Web site within the next few days. As noted in the comments, we ask that API advise the Agency, within 60 days of this posting on the Web site, of any modifications to its submission. Please send any electronic revisions or comments to the following e-mail addresses: oppt.ncic@epa.gov and chem.rtk@epa.gov.

If you have any questions about this response, please contact Dr. Ralph Northrop, of the HPV Chemicals Branch, at 202-564-7666. Submit questions about the HPV Challenge Program through the "Contact Us" link on the HPV Challenge Program Web site pages or through the TSCA Assistance Information Service (TSCA Hotline) at (202) 554-1404. The TSCA Hotline can also be reached by e-mail at tsca-hotline@epa.gov.

I thank you for your submission and look forward to your continued participation in the HPV Challenge Program.

Sincerely,

/s/

Oscar Hernandez, Director
Risk Assessment Division

Enclosure

cc: W. Penberthy
M. E. Weber

EPA Comments on Chemical RTK HPV Challenge Submission:
Reclaimed Substances Categories
(Streams Containing Naphthenic Acids, Phenolics, Disulfides, and Acids or Caustics)

Summary of EPA Comments

The sponsor, the American Petroleum Institute, submitted a test plan and robust summaries to EPA for "reclaimed substances" dated December 15, 2003. The submission includes four categories of petroleum streams covering 12 CAS numbers. EPA posted the submission on the ChemRTK HPV Challenge Web site on January 20, 2004.

EPA has reviewed this submission and has reached the following conclusions:

1. Scope of EPA comments. These comments evaluate the submitted information on the napthenic acids category and the grounds for excluding the acids/caustics category from testing consideration. EPA will address the phenolics and disulfides issue in separate correspondence as is normally done for "no longer HPV" requests.

2. Category Justification. Naphthenic Acids: The category is reasonable for the health and environmental effects endpoints. Acids or Caustics: The grouping of these substances is supported by their status as wastes, their extreme pH values and their corrosive potential.

3. Physicochemical Properties and Environmental Fate. The data provided for these endpoints (except fugacity) are adequate for the purposes of the HPV Challenge Program. The submitter needs to provide fugacity data relevant to the sodium naphthenates stream.

4. Health Effects. Naphthenic Acids: The submitted data on acute toxicity are adequate for the purposes of the HPV Challenge Program. EPA agrees with the proposal to perform a combined repeated-dose/developmental/reproductive toxicity screening test incorporating a micronucleus test, using naphthenic acid to address these endpoints. EPA encourages the submitter to obtain specific information from the National Toxicology Program (NTP) about the cited genetic toxicity data. Acids or Caustics: EPA agrees that testing would not provide useful information.

5. Ecological Effects. Naphthenic Acids: EPA agrees with the submitter's proposal to test naphthenic acid on all ecological endpoints. Acids or Caustics: EPA agrees that testing would not provide useful information.

EPA requests that the submitter advise the Agency within 60 days of any modifications to its submission.

EPA Comments on the Reclaimed Substances Challenge Submission

General

The submission inappropriately refers to "subcategories", and the treatment of four categories in one document adds further confusion as to the submitter's intent. Chemical structures are lacking.

Category Definition

Naphthenic Acids. The naphthenic acids, sodium salts (CAS No. 61790-13-4) and crude naphthenic acids (petroleum) (CAS No. 64754-89-8), represent intermediate steps/streams formed during the refining of petroleum distillates to the commercially viable naphthenic acids (CAS No. 1338-24-5).

The sodium salts (naphthenates) in CAS No. 61790-13-4 are typically in concentrations of 5-15%, with 0-0.5% sodium mercaptides and 3-4% sodium hydroxide (pH > 12). Acidification provides the crude naphthenic acids (petroleum), and further refining steps provide the naphthenic acids, predominantly alkyl-substituted cycloaliphatic carboxyl acids having single or fused multiple cyclopentane or cyclohexane rings. Minor components are aromatic, olefinic, hydroxy and dibasic acids. No representative chemical structures for naphthenic acids were included, making it impossible to understand the descriptions of the substances modeled in the physicochemical property robust summaries such as "3-ring cyclohexane." The category definition is not adequate in the absence of appropriate chemical structure examples.

Acids or Caustics. This category includes one acidic waste stream (90-93% sulfuric acid), obtained from refinery recycling plants, and two spent caustic streams. The category definition is adequate.

Category Justification

Naphthenic Acids. The submitter bases the grouping of the category members on their naphthenic acid content (free acid or sodium salt). The submitter states that since all of the streams contain naphthenic acids or salts and it anticipates that the majority of exposures will be to isolated naphthenic acids, "information on the health and environmental effects of naphthenic acids can be extrapolated to the two intermediate streams" that include sodium naphthenates and crude naphthenic acids. No information was presented in the test plan about the potential impact of differences in composition on health or environmental effects. In addition, the submitter did not state whether the physicochemical or environmental fate properties of the members were similar or displayed a pattern, but specifically stated that physicochemical data on naphthenic acids would be used to represent the category.

The physicochemical and fate properties of the intermediate sodium naphthenates stream components will differ from those of the acids. However, from a practical testing standpoint, this issue is not significant (see test plan section below).

For health effects endpoints, the submitter focused on the free acid form of naphthenic acids for fulfilling the testing needs of the category. This focus is most reasonable under conditions where the spent streams are diluted and/or neutralized, whereby the toxicological data for the acids are expected to be representative of the salts in the diluted naphthenate stream. Thus, although differences would exist, expected similarities in the toxicological properties of these substances can justify their grouping into a category.

Data provided for naphthenic acids indicate that these acids are "moderately to highly toxic" to aquatic species. EPA agrees that these data will apply to both the free acid and sodium salt forms of the napthenic acids and therefore support the category.

Overall, since the naphthenic acid streams in this category share a common process pathway and the data provided for isolated naphthenic acids will likely be representative of the other members for health and environmental effects, the grouping of the members into a category is supported for these endpoints.

Acids or Caustics. The submitter noted that the category members are highly acidic or highly basic by-products of various petroleum refining processes. EPA agrees that the members of this category have extreme pH values and corrosivity.

Test Plan

Physicochemical Properties (melting point, boiling point, vapor pressure, partition coefficient and water solubility)

The data supplied by the submitter for naphthenic acids are adequate for the purposes of the HPV Challenge Program, if representative chemical structures are provided (see Category Definition, above).

These data should not be used to represent the sodium naphthenate stream. Salts in this stream are expected to have markedly different physicochemical properties than the corresponding free acid (e.g., increased boiling point, vapor pressure, and water solubility values). While the submitter has not specifically addressed these endpoints for the sodium naphthenate stream, further testing would generally not provide meaningful data because of the compositional complexity of the mixture (melting point, water solubility, log Kow), because they likely miss OECD testing thresholds (boiling point, vapor pressure), because of limiting properties (photodegradation), or combinations of these.

Vapor pressure. From the submitter's estimates for various cycloaliphatic naphthenic acids, some commercial naphthenic acid mixtures containing mainly lower molecular weight components may have vapor pressures above the HPV testing threshold of 10^{-5} Pa ($7.5x10^{-8}$ mm Hg), but it is unlikely that testing will provide more useful data.

Water solubility. Estimated water solubility values ranged from 0.002 mg/L for a 2-ring cyclohexane to 2.1 mg/L for a 4-ring cyclohexane. The submitter needs to address the 1000-fold difference for chemicals with nearly identical molecular weights. Although some commercial naphthenic acid mixtures may have water solubilities greater than the 1 ppb testing threshold, it is unlikely that additional test data will be useful.

Environmental Fate (photodegradation, stability in water, biodegradation, fugacity)

The data provided by the submitter for naphthenic acids for photodegradation, stability in water, and biodegradation are adequate for the purposes of the HPV Challenge Program, with the addition of suitable representative chemical structures. These data should not be used to represent the sodium naphthenates; however, for reasons given earlier, testing would not provide meaningful data.

Biodegradation. The results presented indicate that some simple naphthenic acids may be biodegradable, but many compounds in this mixture appear to resist aerobic biodegradation. EPA located a reference in which Morales et al. (1993) observed that the rate of biodegradation of individual naphthenic acids decreases with increasing number of carbons (especially >17) and with an increasing degree of cyclization. Because the category represents complex mixtures of naphthenic acids, further testing is unlikely to provide useful data. However, the submitter needs to explain why all the tested single compounds, which have the carboxyl group attached directly to the ring, are considered representative when, according to the test plan, "[t]he carboxyl group is usually attached to a side chain rather than directly to the ring."

Fugacity. The submitter estimated the fugacity of naphthenic acids using a Level I model. EPA believes that values based on a Level III fugacity model are more realistic and useful for estimating a chemical's fate in the environment. Nevertheless, the submitter's Level I fugacity calculations are adequate for assessment of this endpoint for the free naphthenic acids.

The submitter did not specifically address fugacity for the sodium naphthenate intermediate stream. The salts are likely to have greater mobility in the environment because of their increased water solubility and higher partitioning to water. The data for this stream are inadequate for an assessment of this endpoint and fugacity calculations are needed for assessment of this endpoint for the naphthenate salts.

Health Effects (acute toxicity, repeated-dose toxicity, genetic toxicity, and reproductive/developmental toxicity)

Naphthenic Acids. The acute toxicity endpoint has been addressed for the purposes of the HPV Challenge Program. EPA agrees with the submitter's proposal to perform an OECD 422 test for the repeated-dose, developmental, and reproductive toxicity endpoints. EPA also agrees with the submitter's proposal to incorporate a micronucleus test into the OECD 422 protocol to address the genetic toxicity (chromosomal aberration) endpoint. EPA assumes the test will be performed via the oral route.

Genetic Toxicity. The *in vitro* results for bacterial mutagenicity and chromosomal aberration (including a sister chromatid assay) on naphthenate salts that were cited in the test plan are not adequate because no data summaries were provided. Although the NTP website cited by the submitter did not provide details, EPA encourages the submitter to request the specific information on these studies; if these are unavailable, the submitter will need to conduct appropriate gene mutation testing.

Acids or Caustics. No health effects data were submitted and no testing was proposed. The test plan mentions the highly acidic or caustic nature of the category members, but does not explicitly state a rationale for not testing these materials. EPA believes that testing the members of this category is unnecessary as their toxicological effects will reflect their extreme pH values and corrosivity.

Ecological Effects (fish, invertebrates, and algae)

Naphthenic Acids. EPA agrees with the submitter's plan to conduct OECD-compliant fish, invertebrate, and algal toxicity testing on naphthenic acids.

Acids or Caustics. EPA agrees with the submitter that testing on aquatic organisms is not appropriate.

Specific Comments on the Robust Summaries

Physicochemical Properties

The substances chosen for modeling were not adequately identified, especially in the absence of any chemical structures in the Test Plan. CAS numbers or adequate systematic names are needed.

Health Effects

The robust summaries did not identify or assign CAS numbers to the test materials.

Naphthenic Acids

Reproductive Toxicity. A summary for a one-generation reproductive toxicity assay in rabbits exposed dermally for 10 weeks to calcium naphthenate was derived from a tabulated summary (EPA website summarizing TSCA submissions). The full study is available from the OPPT docket (No. 40-8471080) (http://www.epa.gov/chemrtk/robsumgd.htm). The submitter is encouraged to review this information to determine its relevance given the plan to perform an OECD 422 test.

Developmental Toxicity. A summary for a developmental toxicity assay in rats exposed orally to naphthenic acid was derived from an abstract. Again, the submitter may want to find out more information on the methodology used and the developmental parameters assessed to determine its relevance given the plan to perform an OECD 422 test.

Followup Activity

EPA requests that the submitter advise the Agency within 60 days of any modifications to its submission.

References

Lai, J.W.S., Pinto, L.J., Kiehlmann, E., Bendell-Young, L.I., and Moore, M.M. 1996. Factors that affect the degradation of naphthenic acids in oil sands wastewater by indigenous microbial communities. Environ. Toxicol. Chem. 15: 1482-1491.

Morales, A., Hrudey, S.E., and Fedorak, P.M. 1993. Mass spectometric characterization of naphthenic acids in oil sands wastewaters. Technical Report. Fine Tailing Fundamentals Consortium, Alberta Oil Sands Technology and Research Authority, Edmonton, AB, Canada. (as cited by Lai et al., 1996).